



LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

Modelling and Experimental Studies of the Effect of Water at the Polymer-Filler Interface in Silica-Filled Siloxane Rubbers

L. N. Dinh, M. A. Schilbach, G. B. Balazs, R.
Gee, R. S. Maxwell

August 24, 2004

Filler Reinforcement of Rubber
London, United Kingdom
September 14, 2004 through September 14, 2004

Disclaimer

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

Modelling and Experimental Studies of the Effect of Water at the Polymer-Filler Interface in Silica-Filled Siloxane Rubbers

L.N. Dinh, M.A. Schildbach, G.B. Balazs, R. Gee, & R.S. Maxwell
Lawrence Livermore National Laboratory, Livermore, California, USA

bb@llnl.gov, maxwell7@llnl.gov

tel: 925-423-5403 (Balazs) & 925-423-4991 (Maxwell)

1 INTRODUCTION

Silica-filled polydimethylsiloxane (PDMS) composite systems find a broad range of applications due to their chemical and environmental resilience and the ability to fine tune, through chemical and processing modifications, the chemical and mechanical properties [1-3] resulting in a precise engineering property for the final component. Thus, requirements for, and life-performance predictions of, these materials require an understanding of the interaction between the silica filler and the polymer network. Because silica surfaces are well known to have a high affinity for water adsorption [4-6], and this water is a critical part of the interface between the silica particles and the polymer matrix (see Figure 1), water at this interface has important consequences on the nature of the silica-polymer bonding and subsequently the mechanical behaviour [7].

Previous studies have reported on the water speciation and long-term outgassing kinetics of common fumed and precipitated silicas used in silicone elastomers, and of one such copolymer system in particular [4, 8]. Several different water species were observed to be present with a range of desorption activation energies. The amount and type of species present were observed to be dependent on the thermal and chemical history of the filler and the composite [8].

Solid state Nuclear Magnetic Resonance (NMR) methods [7,9] based on quantification of residual magnetic dipolar couplings have also been applied, as these measurements have been shown to be quite sensitive to dynamic and morphological changes in elastomer systems [10-13]. These residual dipolar couplings in elastomeric materials arise due to polymer network constraints (on the NMR timescale) that prevent the averaging, due to reorientations, of the homonuclear dipolar couplings to zero. Residual dipolar couplings, as a result, can be used to test theories of elasticity, gelation, and polymer conformation. In addition, Molecular Dynamics (MD) investigations have found that the removal of water from the polymer-filler interface has a significant effect on the polymer motional dynamics [14].

2 EXPERIMENTAL AND COMPUTATIONAL METHODS

Experimental studies were performed on composite polysiloxanes consisting of two formulations based on silica-filled polydimethylsiloxane. The first, referred to as M97, is a random copolymer of dimethyl (DMS), diphenyl (DPS), and methyl vinyl (MVS) siloxanes. The percentages of each monomer unit in the base rubber were 90.7 wt.% PDMS, 9.0 wt.% PDPS, and 0.31 wt.% PVMS (NuSil Corp., Carpinteria, CA). This elastomer was compounded into a reinforced gum by milling with a mixture of 21.6 wt.% fumed silica (Cab-o-Sil M7D, Cabot Corporation, Tuscola, IL), 4.0 wt.% precipitated silica (Hi-Sil 233, PPG Industries Inc., Pittsburgh, Pa), and 6.8 wt.% ethoxy-terminated siloxane processing aid (Y1587, Union Carbide Corp, Danbury, CT). After bin aging, this reinforced gum was cured with the addition of a peroxide curing agent. The second siloxane formulation studied is TR-55, a composite from Dow Corning containing 70 wt. % of a proprietary polysiloxane gum formulation and 30 wt.% fumed silica filler pretreated with a silating agent.

To measure the quantity and kinetics of the removal of water from the polymer composites, temperature programmed desorption (TPD) experiments [8] were performed as follows. A thin slice of siloxane rubber (~ 0.14 mm thick) was enclosed in a 1 cm^2 platinum foil envelope, with one side perforated with pin holes over the entire surface and fixed by clamps in an ultrahigh vacuum chamber. Heating of the sample was done by passing current through a tungsten coil located 2 mm behind the sample, and the sample temperature was measured using a type K thermocouple inserted between the Pt envelope front surface and one of the clamps holding the envelope. The perforated side of the Pt sample envelope was located 2 mm from a 6 mm diameter orifice to a separately pumped detector chamber equipped with a quadrupole mass spectrometer. The base pressure in the detector chamber was usually a decade lower than that in the sample chamber. This arrangement guaranteed that only gases originating from the portion of the sample facing the 6 mm orifice contributed to the signals detected by the mass spectrometer.

Polymer chain dynamics were measured using a ^1H NMR spin-echo approach that has been described previously [7,9,15]. A small sample of polymer was sealed in a 5 mm NMR tube with a small amount of desiccant positioned so that only the polymer was within the receiver coil volume; this sample was then aged for up to one year and transverse relaxation times were measured periodically by spin-echo methods. 7 s $\pi/2$ pulse lengths, 7-second relaxation delays, and a standard Bruker 5 mm TBI probe were used on a Bruker DRX-500 NMR spectrometer [Bruker Biospin, Billerica, MA]. The echo decay curves were analyzed by measuring the time to reach $1/e$ of the initial intensity, T_{2e} , after removing the effects of the contribution to the decay of the sol fraction of the polymer ($\sim 10\%$ of the echo decay curve). As has been shown [7,9,15], the relaxation rate, $1/T_{2e}$, is a good measure of relative changes in segmental dynamics, i.e., changes in crosslink density or filler-polymer interaction.

Molecular Dynamics simulations were carried out using three dimensional periodic arrays of orthorhombic unit cells containing one unbranched PDMS polymer chain of 120 dimethylsiloxane monomer units. The PDMS chains were then introduced onto a silica surface with the approximate dimensions of $22\text{ \AA} \times 22\text{ \AA}$, and a thickness of $\sim 15\text{ \AA}$. The actual cell length normal to the silica surface was chosen such that the PDMS interfaced to the silica surface did not interact with its periodic image. The PDMS melt therefore experiences both a solid and vacuum interface. The filler hydroxyl surface concentration ranged between that of a dehydrated silica surface (zero hydroxyl groups) to one with twice the average number of groups per unit area, as determined experimentally [16] (i.e., $\approx 8\text{ OH} / 100\text{ \AA}^2$). Simulations were also performed with a layer of physisorbed water placed at the PDMS / silica interface. The initial polymer starting configurations were generated using a Monte Carlo method [17]. The monomers were allowed to ‘polymerize’ in a head-to-tail manner with no monomer reversals. The resulting amorphous structure along with the silica surface was then relaxed by energy minimization.

3 RESULTS AND DISCUSSION

Thermally Programmed Desorption

Figure 2 shows a typical water temperature programmed desorption (TPD) spectrum for the silica-filled siloxane TR55 after 20-30 minutes of vacuum pumping using a heating rate of 0.1 K/s . Upon integration of the mass 18 signal with respect to time and calibration of the mass spectrometer’s response, the total moisture content of the pumped-down sample was measured to be on the order of 0.35 wt\% . The total moisture content of TR55 in the open air should be this measured 0.350 wt\% , plus any loosely bonded physisorbed water pumped off prior to the start of the TPD experiments. Microbalance experiments show that this pump-down resulted in a weight loss for TR55 of between 0.6 and 0.80 wt\% , although TPD experiments indicated that the removal of species other than water account for the additional weight loss.

In order to predict how much of this moisture would be released from TR55 in dry storage over time, the H_2O desorption spectrum shown in Figure 2 must be deconvoluted into its proper sub-components. This method of analysis and data are reported separately [8]. The deconvolution indicates that the H_2O desorption process in TR55 cannot be adequately

described by a single activation energy process, since the values for the activation energy barrier for the desorption process were found to significantly increase with the desorption fraction. The TPD deconvolution resulted in water species that we have labelled P1 through P8. We associate P1 and P2 with the desorption of water multilayer and water molecules hydrogen bonded to SiOH. P3 to P8 are associated with chemisorbed water molecules formed from the condensation of hydroxyl groups, with hydroxyl density decreasing going from P3 to P8. From the data, we can also predict the removal of water from this composite polymer based on the amount of time that the polymer is exposed to a desiccating environment. Species P1 and P2 completely outgas at room temperature in a dry environment in a matter of a few hours and a few weeks respectively, while only 25 % of the moisture content from P3 and less than 2 % of the moisture content from P4 would be released at room temperature over the next 100 years of dry storage. Therefore, physisorbed water species (P1 and P2) and the more loosely bound chemisorbed water species (P3 and P4) contribute to room temperature outgassing in dry environments to varying degrees while the more tightly bound chemisorbed water species (P4, P5, P6, P7, P8) produce no outgassing on a practical time scale.

Nuclear Magnetic Resonance

Nuclear Magnetic Resonance experiments on siloxane polymer systems have previously been reported by us [7,9,15]. In the present work, we have applied periodic NMR relaxation measurements to samples that were exposed to desiccating agents over the course of several hundred days. ^1H NMR relaxation measurements of transverse relaxation times in this polymer system have been directly correlated to the segmental dynamics of the polymer chains and thus the polymer mechanical properties ($1/T_2 \propto \text{dynamics} \propto \text{crosslink density} \propto G'$). The results of spin-echo relaxation time experiments on a desiccated M97 composite sample are shown in Figure 3. The results indicate that, as the polymer material was aged in the presence of desiccating agents with various relative affinities for water ($\text{LiH} > \text{P}_2\text{O}_5 > \text{molecular sieves}$), the polymer segmental dynamics were seen to slow down over the course of one year. Based on the correlation established previously, this change corresponds to a change in G' after 1 year of $\sim 30\%$. Additionally, the relative stiffening ability of the various desiccating agents was observed to be roughly consistent with their affinities for water.

Molecular Dynamics Modelling

The local dynamics of the M97 polymer, both as a function of hydration level of the silica surface as well as the distance from its surface, were measured using MD simulations. The PDMS motional dynamics were modelled using the following time autocorrelation function (ACF),

$$P_i(t) = \langle \mu(0) \cdot \mu(t) \rangle$$

where $\mu(t)$ is a unit vector and $\langle \rangle$ denotes an ensemble average over all such vectors. The results for the bond vector ACF between the silicon atom in the polymer backbone and the carbon atom of the pendent methyl groups (Si-CH_3) are shown in Figure 4. This figure shows $P_i(t)$ for PDMS at 550 K as a function of the distance from the silica surface at a surface hydration level of $\sim 8 \text{ OH}/100 \text{ \AA}^2$. It can be seen from Figure 4 that the mobility of the polymer near the surface is diminished considerably as compared to those bond vectors found further from the surface. Comparison of the mobility of the polymer matrix at the silica surface to that of the bulk PDMS fluid show that the PDMS relaxation dynamics in the presence of the silica filler is slowed considerably at 550 K. The PDMS dynamics were also found to be affected by the hydration levels of the silica surface. The general trend is that the polymer mobility tends to decrease (increased relaxation times) as the hydration level decreases, thus effectively “stiffening” the polymer matrix. This may be due in part to screening of the long-ranged electrostatic charge by the chemisorbed hydroxyl groups or physisorbed water in the interfacial region.

The motional dynamics of PDMS obtained from our simulations, as a function of hydration level of the silica filler exhibit the same functional trend as identified from NMR as shown in

Figure 3 (see the experimental section above), that is, the relative “stiffness” of the PDMS matrix is found to increase as the hydration level decreases.

4 CONCLUSIONS

The quantity, outgassing, and effects of polymer/filler interfacial water on the structure and dynamics in silica-filled polydimethylsiloxane (PDMS) based composites have been investigated. Temperature Programmed Desorption (TPD) measurements have quantified the amount of water in a TR55 formulation and have allowed the development of predictions of the rate of the removal of water from the interface between the polymer and filler. Nuclear Magnetic Resonance (NMR) experiments have provided information on the polymer motional dynamics as a function of the desiccation of the composite, indicating that the polymer matrix stiffens as water is removed. Molecular dynamics simulations suggest that the polymer-silica contact distance and the mobility of interfacial polymer chains significantly decreased as the hydration level at the interface was reduced. The reduced mobility of the PDMS chains in the interfacial domain reduced the overall, bulk, motional properties of the polymer, thus causing an effective "stiffening" of the polymer matrix.

This work was performed under the auspices of the U.S. Department of Energy, by the University of California, Lawrence Livermore National Laboratory under contract No. W-7405-ENG-48.

REFERENCES

1. G. Kraus, *Rubber Chem. Tech.* **38**, 1070 (1965).
2. J. M. Zeigher, F. W. G. Fearon, *Silicon Based Polymer Science: A Comprehensive Resource*, Vol. **224**, ACS Press (1990).
3. P. Vondracek, A. Pouchelon, *Rubber Chem. Technol.* **63**, 202 (1990).
4. L. N. Dinh, M. Balooch, J. D. LeMay, *J. Colloid Interface Sci.* **230**, 432 (2000).
5. V. M. Gun'ko, V. I. Zarko, B. A. Chuikov, V. V. Dudnik, Yu. G. Ptushinskii, E. F. Voronin, E. M. Paklov, A. A. Chuiko, *Inter. J. Mass Spectrom. Ion Process.* **172**, 161 (1998).
6. A. Feng, B. J. McCoy, Z. A. Munir, D. E. Cagliostro, *J. Colloid Interface Sci.* **180**, 276 (1996).
7. R. S. Maxwell, B. Balazs, *J. Chem. Phys.* **116**, 10492 (2002).
8. L. N. Dinh, M. A. Schildbach, R. S. Maxwell, W. J. Siekhaus, G. B. Balazs and W. McLean II, *J. Colloid Interface Sci.*, **274**, 25 (2004).
9. R. S. Maxwell, G. B. Balazs, *Nucl. Inst. and Meth. in Phys. Res. B* **208**, 199 (2003).
10. J. P. Cohen-Addad, *Prog. NMR Spect.* **25**, 1 (1993).
11. W. Gronski, U. Hoffmann, G. Simon, A. Wutzler, E. Straube, *Rubber Chem. Tech.*, **65** 63 (1992).
12. E. Fischer, F. Grinberg, R. Kimmich, S. Hafner, *J. Chem. Phys.* **109**, 846 (1998).
13. F. Grinberg, M. Garbarczykm, W. Kuhn, *J. Chem. Phys.* **111**, 11222 (1999).
14. R. H. Gee, R. S. Maxwell, G. B. Balazs, *Polymer* **45**, 3885 (2004).
15. A. Chien, R. S. Maxwell, D. Chambers, G. B. Balazs, *Rad. Phys. Chem.* **59**, 493 (2000).
16. D. Bordeaux, J. P. Cohen-Addad, *Polymer* **31**(4), 743 (1990).
17. Molecular Simulations, Inc., San Diego, CA.

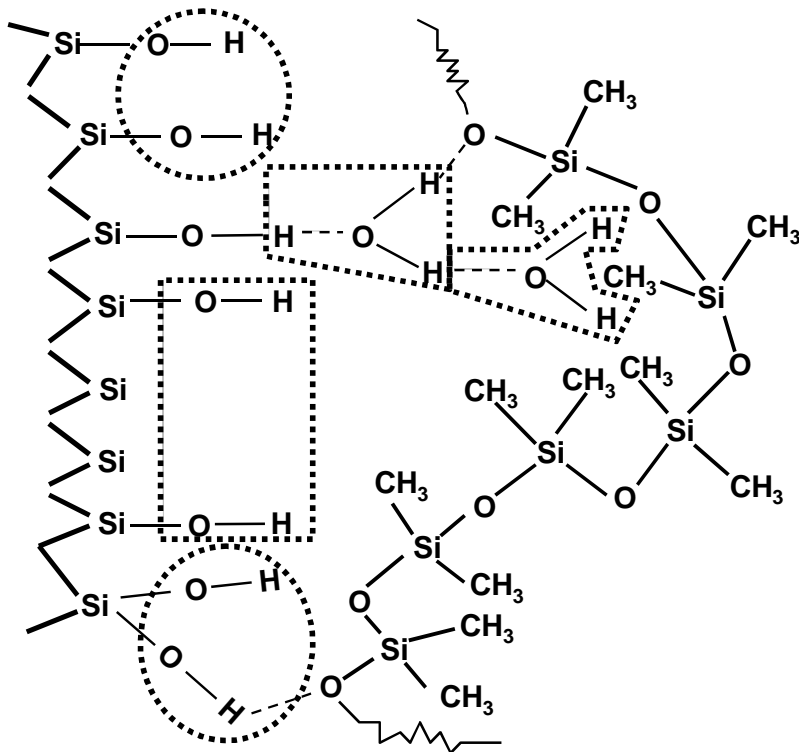


Figure 1. Schematic representation of water species (indicated in boxes) at the interface of the silica filler surface (on left) with the PDMS polymer chain (on right).

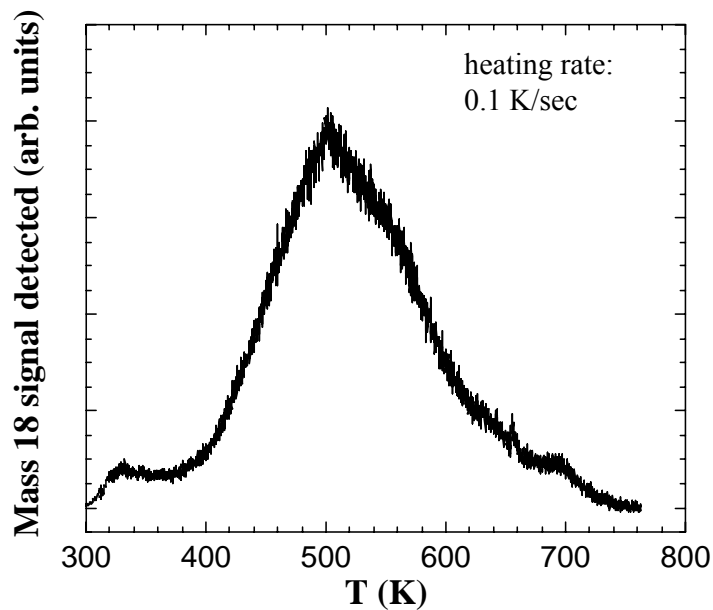


Figure 2. A typical water TPD spectrum of TR55 polymer composite at a heating rate of 0.1 K/s

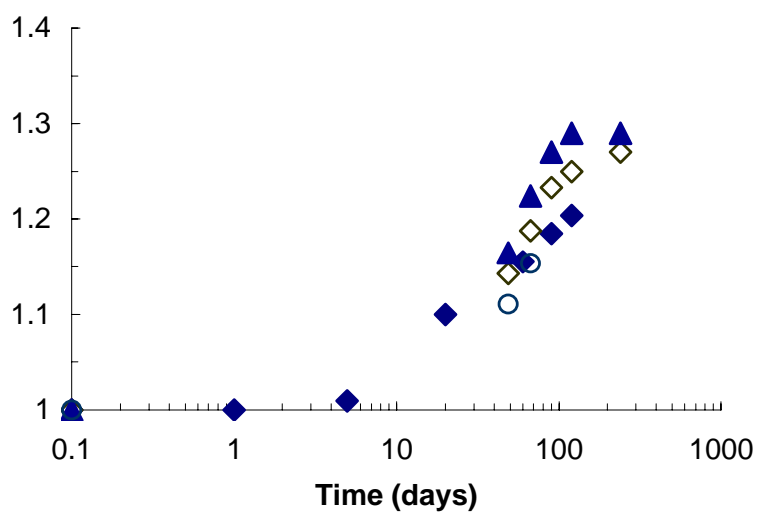


Figure 3. Relative stiffness of M97 polymer composite as a result of desiccation in the presence of P_2O_5 , LiH, and molecular sieves, as measured by NMR relaxation methods.

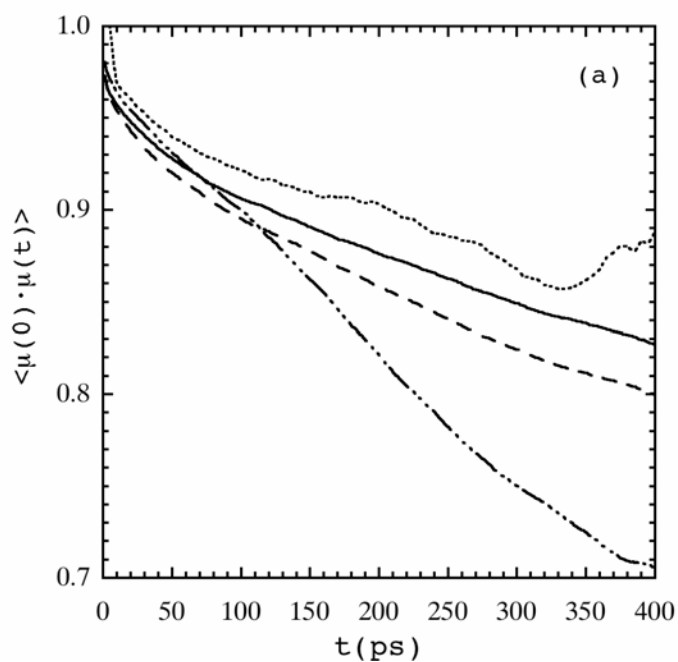


Figure 4. The decay of $P_I(t)$ at 550 K showing decay for those PDMS $Si-CH_3$ bond vectors closest to the silica surface as a function of surface hydration: dehydrated (dotted), ~ 4 OH/100 \AA^2 (solid), ~ 8 OH/100 \AA^2 (dashed), and physisorbed water at surface (dash-dotted).